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14. ABSTRACT

We have demonstrated the growth of Tm and Lu doped LaAlO3 epitaxial thin films on single crystal (001) SrTiO3 substrates. These rare-earth dopants potentially act as sources of localized moment and spin-orbit scattering centers at the interface. Through structural and chemical characterization, we confirm the incorporation of Tm and Lu dopants into highly crystalline LaAlO3 films. The rare earth doping of the La site does not significantly modify the sheet carrier concentration or mobility compared to undoped samples despite the evolution of sheet carrier

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ABSTRACT

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Quasi-two-dimensional electron gas behavior in ...

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Quasi-two-dimensional electron gas behavior in doped $LaAlO_3$ thin films on $SrTiO_3$ substrates

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We have demonstrated the growth of Tm and Lu doped $LaAlO_3$ epitaxial thin films on single crystal (001) $SrTiO_3$ substrates. These rare-earth dopants potentially act as sources of localized moment and spin-orbit scattering centers at the interface. Through structural and chemical characterization, we confirm the incorporation of Tm and Lu dopants into highly crystalline $LaAlO_3$ films. The rare earth doping of the La site does not significantly modify the sheet carrier concentration or mobility compared to undoped samples despite the evolution of sheet carrier concentration, mobility, and sheet resistance with $LaAlO_3$ thickness in undoped $LaAlO_3$ films on $SrTiO_3$. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4800232]

With the demonstration of metallicity at the interface of the band insulators $LaAlO_3$ (LAO) and $SrTiO_3$ (STO),[1] there have been many subsequent studies exploring the mechanism behind this metallicity. It is now generally agreed upon that interfacial metallicity can be generated through the epitaxial growth of LAO films on TiO_2 terminated (001) STO under the appropriate growth conditions.[2–5] These results are largely possible due to advances in complex oxide deposition techniques allowing for thin film growth of near atomic scale accuracy. The quasi-two-dimensional gas at the interface of LAO/STO is rich in phenomena, with reports of superconductivity, magnetic ordering, and strong spin orbit coupling.[6–11]

There has been some effort in generating additional functionality in this quasi-two-dimensional electron gas by doping at the interface and away from the interface, often referred to as remote doping. Fix *et al*. have doped the STO with small amounts of Co and Mn ions in an attempt to create a modified quasi-two-dimensional electron gas.[12] Substitution of the transition metal ions appears to result in aliovalent doping which modifies the carrier concentration and overall transport behavior. More recently, Fix *et al*. have used remote doping of Mn ions to identify that most of the carriers in the electron gas appear to come from the STO at the interface.[13,14]

While carriers in the quasi-two-dimensional electron gas at the LAO/STO interface appear to reside in the STO,[15] there is evidence that the properties of the LAO side of the interface also affect the metallic transport. Early reports cited a step function in the carrier concentration and conductivity above a critical LAO thickness.[5] More recent studies found that the sheet resistance, carrier concentration, and mobility depend on the LAO thickness, thus suggesting that the LAO plays some role in the conduction.[4] Moreover, we have previously shown that the thickness of LAO plays a role in tuning the disorder and localization in the quasi-two-dimensional electron gas through a series of magnetotransport measurements.[10]

In this paper, we report on the synthesis and characterization of LAO/STO interfaces where Tm and Lu dopants are substituted onto the La site of the LAO film in order to investigate the role of the LAO in the metallic transport and to explore the insertion of strong spin-orbit interaction and magnetic moment into the LAO side of the LAO/STO system. These Tm^{3+} and Lu^{3+} ions are isovalent dopants that preserve the nature of the charge carriers while introducing strong spin-orbit scatterers and/or local magnetic moments at and near the LAO/STO interface. Compared to the undoped samples, we find that these dopants modify the carrier concentration and mobility to a limited extent. The modest decreases in the carrier concentration and increases in mobility indicate that scattering in the quasi-two-dimensional electron gas is not affected significantly by the presence of magnetic or spin-orbit scatterers in the LAO.

Pulsed laser deposition was used to grow thin films of $(La_{0.98}Tm_{0.02})AlO_3$ and $(La_{0.98}Lu_{0.02})AlO_3$ on $SrTiO_3$ (STO) substrates. Single crystal (001) STO substrates were etched in buffered hydrofluoric acid and annealed for 2 h at 1000 °C in air in order to obtain smooth TiO_2 termination. Polycrystalline targets of 2% Tm and Lu doped LAO were used to deposit epitaxial thin films with a KrF laser operating at 2 Hz and 1.3 J/cm^2. The substrates were held at 700 °C during deposition in a 3.0×10^{-5} Torr of oxygen atmosphere. These conditions do not promote the generation of a significant concentration of defects in the bulk of the STO that may affect sample transport properties.[3] A PANalytical X'Pert X-ray Diffractometer was used to perform 2θ–θ and ω scans as well as reciprocal space maps. Rutherford backscattering spectrometry (RBS) was used to determine sample thickness as well as composition. The sample thickness values were also confirmed with X-ray reflectivity

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measurements. Composition of the Tm doped samples was confirmed with X-ray absorption spectroscopy (XAS) performed at grazing incidence (i.e., incident X-ray beam at 30° from the film surface) at beamlines 6.3.1 and 4.0.2 of the Advanced Light Source. A Quantum Design Physical Properties Measurement System was used for all of the electrical transport measurements. These measurements were performed in the van der Pauw geometry with the applied magnetic field of up to 7 T orthogonal to the interface (out of plane). Magnetic characterization was performed using a Quantum Design SQUID magnetometer and X-ray magnetic circular dichroism (XMCD) at beamline 4.0.2 of the Advanced Light Source.

We have synthesized epitaxial Tm and Lu doped LAO thin films on (001) STO substrates to form a quasi-two-dimensional electron gas at the film-substrate interface. X-ray diffraction indicates that the doped LAO films grow epitaxially on (001) STO with only evidence for (00l) family of film peaks in the θ-2θ scans. ω scans of the film peaks show typical full width half maximum values of $\Delta\omega < 0.15°$, thus suggesting excellent crystallinity of the films. The degree of crystallinity, as described by $\Delta\omega$, and the lattice parameters were not modified to any detectable degree by the presence of dopants. In order to confirm the intentional doping of the LAO films, we performed RBS and XAS. The RBS spectra were fitted for atomic composition and film thickness, and by comparing the experimental data to the simulation, we find that, similar to the target used for pulsed laser ablation, Tm or Lu can be found in the film at approximately 2 at. % doping. In Fig. 1, an X-ray absorption (XA) spectrum of the same Tm doped sample indicates absorption at the M_5 edge of Tm; however, the fully occupied f shell of Lu precluded the observation of a Lu M_5 edge in XAS. Only the M_5 edge of Tm is seen here as the M_4 edge has been observed to be 20 times weaker than the M_5.[16]

We explored the magnetic response of doped LAO/STO samples through both SQUID magnetometry and XMCD. Magnetic inhomogeneities and ferromagnetism at the LAO/STO interface have been predicted in theory and reported by some.[6,8,9] Through doping with local magnetic moments on the LAO side of the interface in the form of 2 unpaired 4f electrons in Tm^{3+}, we explored the possible generation of magnetic response at the interface. However, SQUID magnetometry showed no evidence for any magnetic transition in the temperature dependence of the magnetization. Likewise magnetic hysteresis in the Tm doped films was not statistically significant down to 7 K. XMCD measurements, however, detected a significant magnetic response of the Tm atoms in an applied 0.5 T field at 20 K as seen in Fig. 1. The magnetic origin of this circular dichroism signal was confirmed by monitoring the polarization dependence of the XA spectra. The spin and orbital magnetic moments were calculated using the sum rules for 3d to 4f transition that enable us to estimate $\langle S_z \rangle$ and $\langle L_z \rangle$ as -0.06 and -0.1, respectively.[17–19] The magnetization of the sample is then obtained from $M = -n(2\langle S_z \rangle + \langle L_z \rangle))\mu_B$, where n is the Tm atomic density, and the magnetic susceptibility is extracted assuming a linear field dependence up to 0.5 T. The observed dichroism corresponds to a magnetic susceptibility of 0.002. Assuming the molar mass and density of bulk LAO, we deduce a molar magnetic susceptibility of approximately 3 cm^3/mol. The dichroism suggests a paramagnetic response as no significant hysteresis was observed and the susceptibility is about an order of magnitude higher than the susceptibility of paramagnetic Tm_2O_3.[20,21] Interestingly no dichroism appeared at the Ti $L_{2,3}$ edge of either doped or undoped samples, suggesting that any magnetic ordering present in these samples at 20 K is below the noise threshold of our measurement. Nevertheless, the magnetic response of the Tm atoms observed in XMCD confirms the incorporation of local magnetic moments to the system. While long-range magnetic ordering in the system is not ruled out by these observations, evidence for such ordering is not observed with bulk magnetometry or XMCD in the temperature range explored here.

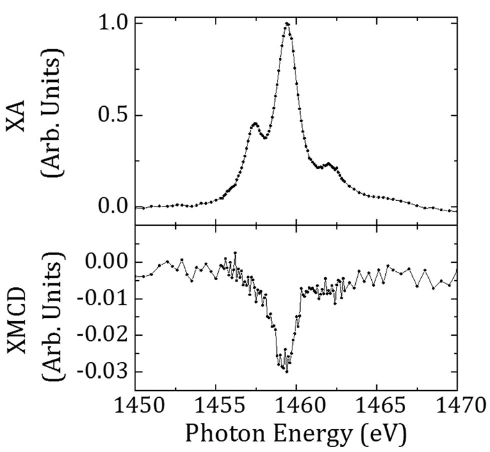

FIG. 1. Chemical and magnetic characterization of a 1.5 nm thick Tm doped LAO film through XAS and XMCD at 15 K. XAS (above) shows the M_5 transition of Tm. XMCD (below) demonstrates magnetic response from the Tm ions in the film in an applied field of 0.5 T.

Through electronic transport measurements, we probed the sheet resistance, sheet carrier concentration, and mobility of Tm and Lu doped LAO films approximately 10 nm thick on STO and compared them to their undoped counterparts. The sheet resistance as a function of temperature in Fig. 2(a) shows that the metallic behavior of the undoped LAO/STO interface is preserved in the doped films. At low temperatures, there is a resistivity upturn in all three types of samples which suggests weak localization. The characteristic temperature for these resistivity minima is unaffected by doping, suggesting that the dopants do not significantly affect the scattering time or trap charge carriers. Though the conduction channel has been reported as lying on the STO side of the interface, one might expect that the introduction of dopants in the LAO film would lead to increased disorder at the interface. Therefore, it is surprising to find that the low temperature mobility, which should be dominated by disorder scattering and localization effects, is not significantly suppressed by doping. In fact, the doped films have equivalent or higher mobilities at low temperatures (Fig. 2(c)) accompanied by lower carrier concentrations (Fig. 2(b)). These two factors combine to provide overall slightly lower sheet resistance values for the doped samples compared to the undoped films.

A closer look at the temperature dependence of the sheet carrier concentration and mobility highlights the similarities with undoped LAO/STO samples. The sheet carrier concentration increases as a function of increasing temperature and

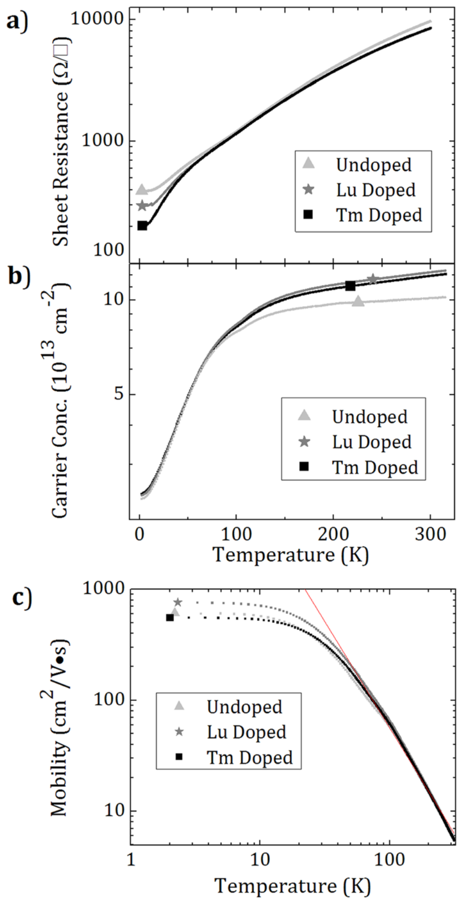

FIG. 2. Temperature dependent behavior of the (a) sheet resistance, (b) sheet carrier concentration, (c) mobility in Tm doped, Lu doped, and undoped films. The carrier concentration roughly saturates at high temperatures to within approximately a third of the value predicted by the polar catastrophe. The mobility is fit to a power law above 60 K indicating the dominance of phonon dependent scattering. Note that the doped films do not lead to appreciably lower mobility at low temperature where defects would be expected to dominate the scattering.

appears to roughly saturate at higher temperatures. The mobility is highest at low temperature where it is dominated by impurity scattering and decreases via a power law dependence associated with phonons. The qualitatively similar magnitude and temperature dependence of the mobility and sheet carrier concentration suggest that the Tm and Lu dopants do not significantly modify the quasi-two-dimensional electron gas.

Despite the presence of Tm and Lu in our doped LAO films, the doping does not appear to dramatically change the thickness dependence of the electronic transport. While past experiments have indicated that the conducting channel lies on the STO side of the interface, numerous studies have shown that the LAO thickness affects many aspects of the transport.[4,5,10,15] As with undoped LAO/STO interfaces, the high-temperature carrier concentration of our doped films depends strongly on the film thickness. After the critical thickness of 4 unit cells of LAO is reached, the carrier concentration rapidly increases with film thickness up to about 20 unit cells where the carrier concentration appears to saturate near 1.2×10^{14} e^-/cm^2 as seen in Fig. 3. This saturation value is about 1/3 of the $1/2$ electron per unit cell value predicted from the polar catastrophe scenario.[22] This behavior is consistent

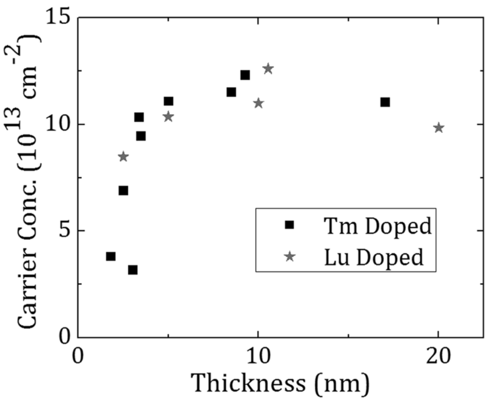

FIG. 3. Thickness dependence of the carrier concentration at 300 K for Tm and Lu doped $LaAlO_3$ films on $SrTiO_3$.

with an equilibrium electric potential balanced by progressive charge transfer to the STO with increasing LAO thickness after the Zener breakdown.[23,24] The evolution of the sheet carrier concentration is clear evidence that the LAO has a significant effect on the electronic behavior of the quasi-two-dimensional electron gas. However, the Tm and Lu dopants provide only a small decrease in the sheet carrier concentration. We would also expect the addition of Tm^{3+} and Lu^{3+} dopants to increase disorder and hence decrease mobility, but we observe the opposite to be true. The small decrease in carrier concentration values and small increase in mobility values may be an indication that small variations in sample quality undetectable by standard structural and compositional characterization may give rise to significant variation in electronic behavior.

In summary, we have demonstrated incorporation of 2% Tm and Lu dopants into epitaxial LAO films grown on TiO_2 terminated STO. The doped LAO films grown on STO substrates exhibit excellent crystallinity and metallic behavior at the interface. Doping with heavy elements does not significantly modify the sheet resistance, sheet carrier concentration, mobility, or their temperature dependence. The evolution of the carrier concentration with doped LAO thickness is similar to that of the undoped case and points to the non-negligible role of the LAO in the transport. However, the Tm and Lu dopants do not significantly affect the transport or enhance any magnetic response.

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